

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Camarota et al.
Serial No.: 09/521,074
Filed: March 7, 2000

Group Art Unit: 1714
Examiner: Anthony, J.D.

Title: **Flame Retardant and Smoke Suppressive Additive Powder for Polymeric Thermoplastics and Thermoset Resins**

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Dirk Brinkman

PROPOSED Amendment ONLY

Assistant Commissioner for Patents
Washington, DC 20231
Sir:

This amendment is in response to an Office Action mailed January 14, 2003.
Please enter this amendment before reconsidering the application.

Claims

1. (currently amended) A flame retarding and smoke suppressing additive powder, comprising, by weight:

a carbonific material 10.0-12.0%;

a heat activated blowing agent 15.5-17.5%;

a heat activated halogen material 12.0- 17.0% which forms a fire extinguishing halogen gas under heat;

a phosphate material 30-33.4% which forms water and phosphorous acid when reacting with ~~one or more~~ of the remaining ingredients in the powder under heat; and

an inorganic binder 23.50-29.5%, the inorganic binder including calcium aluminate cement and silica flour.

2. (previously amended) The powder of claim 1 wherein the carbonific material is selected from the group consisting of dipentaerythritol, pentaerythritol polyurethane, phenol, triethylene glycol, resorcinol, inositol, sorbitol, dextrin, and starch.

3. (original) The powder of claim 1 wherein the heat activated blowing agent is selected from the group consisting of urea, butyl urea, dicyandiamide, benzene sulfonyl-hydrazide, melamine, chloroparaffin, guanidine, and glycine.

4. (previously amended) The powder of claim 1 wherein the heat activated halogen material is selected from the group of chlorinated paraffin by weight - 40% and chlorinated paraffin by weight - 70%.

5. (original) The powder of claim 1 wherein the phosphate material is selected from the group consisting of ammonium polyphosphate, tris(2,3-dibromopropyl) phosphate, tris(beta-chloroethyl) phosphate, guanidine phosphate, urea phosphate, melamine phosphate, monoammonium phosphate, diammonium phosphate and mixtures thereof.

6. (cancelled)

new
issue
because of
addition of
calcium
aluminate
cement and
silica flour
were never
checked in
cancelled claim
6.

12. (currently amended) A flame retarding and smoke suppressing additive powder for mixing with resins comprising, by weight:

10.0-12.0% of a carbonific comprising of dipentaerythritol, dipentaerythritol, pentaerythritol, pentaerythritol polyurethane, phenol, triethylene glycol, resorcinol, inositol, sorbitol, dextrin, and starch;

15.5-17.5% of a blowing agent comprising malamine;

12.0- 17.0 ~~19.0~~% of a halogen containing materials comprising chlorinated paraffins;

30-33.4% of a phosphorous containing material which is selected from the group consisting of ammonium polyphosphate, tris(2,3-dibromopropyl) phosphate, tris(beta-chloroethyl) phosphate, guanidine phosphate, urea phosphate, melamine phosphate, monoammonium phosphate, diammonium phosphate, and mixtures thereof; and

23.5-29.5% of an inorganic material selected from the group consisting of calcium aluminate cement; and silica flour; ~~and glass beads.~~

Remarks

The application was filed with claims 1-12. Claims 7-11 have been withdrawn without prejudice. Claims 1-6, and 12 have been examined and are pending. Claims 1-6, and 12 are rejected. All rejections are traversed. Claim 1 is amended to include elements of cancelled claim 6, and claim 12 is amended to correct Markush groupings separate by -and-. None of the amendments are made to change the scope of what is claimed. No new matter has been introduced into the claims.

In paragraph 1, the Examiner makes the restriction on non-elected claims final.

In paragraphs 2-3, the Examiner rejected claims 1-6, and 12 under 35 U.S.C. 112, second paragraph.

With respect to claim 1, what is claimed is "a carbonific material," "a heat activated blowing agent, ... and a heat activated halogen material which forms a fire extinguishing halogen gas under heat."

Those of ordinary skill in the art would understand that any compound that includes the element carbon, e.g., *all* organic compounds, that breaks down under extreme heat will function, in part, as a carbonific, this is an

unavoidable fact of chemistry, but not a basis for rejecting a claim as being indefinite. Chemist would understand this known secondary reaction, and this is so explained in the specification. However, the unpreventable secondary reaction is not claimed.

Similarly, any compound that includes the elements hydrogen and oxygen, under heat can produce as an intermediate product water (H₂O), which will subsequently vaporize and function, in part, during a secondary reaction as a blowing agent. This reaction is explained in the specification. However, the secondary reaction is not claimed.

The Examiner's comments suggest a rejection on the basis of being indefinite, any intumescent power that has more than one constituent part including carbon, and more than one constituent part containing hydrogen and oxygen, other common elements, because those parts would have "overlapping functions."

Examiner's rejection would have to reject most intumescent compounds, for example, carbon dioxide and paraffin, merely because these contains carbon, which would contribute to the carbonific char layer, and any alcohol or ethol based parts because they contain hydrogen and oxygen, which would contribute to the blowing agent.

For that matter, the Applicants are hard pressed to come up with any material which *does not* turn to a gas when heated by exposure to open flame or high radiant heat, and therefore "acts" like a blowing agent or a gas. Natural physics demands that solids turn to gas when heated, and that various components overlap each other in function. It is well know that any material, under the appropriate temperate and pressure conditions, can be either a solid, a liquid, or a gas, or combinations thereof.

Wrong! → The Examiner provides no evidence that a halogen is a carbon. The fact that it can "act" as a carbonific does not mean that it is. Nowhere, does the application or claims state that "the heat activated blowing agent can act as a carbonific material," quoting the Examiner, in contrast, see at page 7, lines 8-14 "**Blowing Agent** - The blowing agent is primarily comprised of melamine. Heat decomposition of the melamine produces ammonia, urea, water, carbon dioxide, etc. These gases act to expand the volume of the resin during combustion. The gases help produce a multicellular foamy resin which

insulates and protects the resin and structure from additional heat.”

Furthermore, this paragraph makes it quite definite that the function of the blowing gas is to foam and provide insulation from heat.

Claims 1 has been amended to correct “23.5-29.5”, and the Markush claim construction in claim 12 is correct, as well the number “17.0”.

In paragraphs 10-11, the Examiner rejected claims 1-6, and 12 under 35 U.S.C. 103(a) as being unpatentable over Vajs et al. and Wortmann et al. (U.S. Patent 4,743,625 and 4,166,743 - “Vajs” and “Wortmann”).

The Examiner admits that Vajs and Wortmann are different from the claimed invention. Moreover, the claimed invention differs in a way that produces unexpected results, see bottom of page 10.

Moreover, the invented compound has unexpected results. The flame spread ratio of the invented material is **less than half** that of prior art compounds, as tested to the ASTM E-162 Surface Flammability Test. The amount of smoke is an amazing **1/100th**, as tested to the ASTM E-662 Smoke Density Test, and as for a physiologically toxic, the claimed intumescent produces **none**. Note, any toxic gas constituents are below the reporting limit as recognized by the U.S. Passenger Rail Requirement when tested to the BSS 7239 Toxic Gas Analysis – a generally accepted Boeing Aircraft Standard. These unexpected results attached.

The toxicity levels prior art Vajs and Wortmann compounds are potentially high. Both Vajs and Wortmann cite the use of dicyandiamide as an expanding agent. Dicyandiamide is the incorrect name for the dimer of cyanamide. Cyanamide is a cyanide (CN) compound and upon a combustion decomposition toxic vapors of cyanide and cyanide compounds such as hydrocyanic acid (HCN) can be emitted.

The patent Vajs is 24 years old and Wortmann is 15 years old, at that time the use of those toxic compounds was common. However, the acceptable toxicity levels have been reduced considerable since then. For example, upon combustion, new maximum environment toxicity test protocols, such as the Boeing Standard BSS 7239, have a requirement limit of less then 150 ppm of HCN for materials that can be used for U.S. passenger vehicles for interior use. It is unlikely either patented material could pass this universally

employed protocol with the Vajs loading his mixture with 17 to 27 parts, and with Wortmann loading coating with as much as 25 parts of these toxic compounds in their compositions.

The physiological effects of exposure to heat in fires and/or the resultant toxic smoke on the compounds of Vajs and Wortmann can result in varying degrees of incapacitation, permanent injury or death. Visual obscuration and painful irritation of the eyes can impair or reduce the efficiency of egress due to psychological and/or physiological effects. Breathing difficulties, lung inflammation, narcosis and respiratory tract injury, are physiological hazards potentially present in fire scenarios. Narcotic gases, e.g., carbon monoxide, hydrogen cyanide and reduced oxygen, can affect the nervous and cardiovascular systems, causing confusion, a period of intoxication, followed by a collapse and loss of consciousness, followed ultimately by death from asphyxiation.

Those of ordinary skill would appreciate that any compound with **zero reportable** toxicity is extremely significant and desirable. The Examiner has not provided any prior art reference with results that are in any way similar to those of the invention. The unique mixture of the invention achieve both flame retardance and unexpected low levels of toxicity.

NOT True
Vajs at column 4, line 48 and column 5, section 7, discusses a vitrifying material or agent. The Examiner goes on to equate the Vajs vitrifying material to the claimed cement-like inorganic binder. Those of ordinary skill in the art would never confuse cement with glass. A brittle glass can clearly be distinguishable from the hard cementitious inorganic binder including calcium aluminate cement and silica flour.

The definition of *vitrify*: "To change or make into glass or a similar substance, especially through heat fusion." It comes from the Latin vitrum - glass and facere - to make. In the strict sense, glass is a state of inorganic matter that is noncrystalline and amorphous.

The Vajs patent in column 5, Section 7, describes: a vitrifying agent which *locks* the intumescent protective layer ... by vitrifying and when exposed to a temperature. Section 8 specifies the vitrifying, glass forming candidate chemicals specifically. However, borates and silicates of Vajs typically melt together, at relatively low temperatures, between 300 and 350° C.

to form brittle, fragile matrices. The fragile matrices produced by Vajs' mixture adds **no** structural integrity to the char layer profile.

Vajs does not contain a cementitious inorganic binder, e.g., calcium aluminate cement and silica flour, which reacts with water, to form a typical hydrolic cement to add structural integrity to the char layer profile. The strong integral cementitious binder is distinguished from the brittle vitrious binder of Vajs.

Applicants respectfully request which parts at column 4, lines at lines 43-50, "Suitable additives to be added to a product comprise by weight: 7 to 40 parts of ammonium or diammonium phosphate; 17 to 37 parts of pentaerythritol; 17 to 27 parts of dicyandiamide; and 5 to 50 parts of a suitable **vitriifying** material. In addition, 5 to 50 parts of chlorinated paraffin may be added," cited by the Examiner, are believed to be the claimed "*inorganic binder including calcium aluminate cement and silica flour.*"

The Examiner's equating of the Vajs vitrifying material to the claimed cementitious martial is strictly incorrect. A glass is not a cement.

In order to understand the chemistry that lies behind the claimed invention, the following is provided.

The material constituent recipe of the claimed novel inorganic binder system, working in conjunction with the claimed intumescent chemical powders, is the crux of the uniqueness of the present invention.

When a resin is blended with the claimed fire retarding and smoke suppressing powder, the resin mixture elutes upon the particulate constituents during the mixing phase. The constituents are held within the finished plastic substrate by an encapsulating mechanical bond. As would be apparent to one of ordinary skill in the art, this reaction is not possible with the prior art compositions, particularly, those that contain brittle vitrifying materials. Upon exposure to heat, the unique, unexpected, and nonobvious result of the invention is as follows.

As the plastic substrate of the finished product attempts to combust in the presence of high radiant heat or an open flame, the phosphorus-containing constituent decomposes at the start of the pyrolyzing process releasing a

strong acid by-product. This phosphoric acid that is formed dehydrates the pyrolyzing polymer resin and reacts with the alcohol dipentaerythritol carbonific to form initiator-based esters. This series of reactions and decompositions catalyzes the formation of water and expedites the formation of a cementitious char layer. Halogen gases are also formed and liberated from the chlorinated paraffins.

The blowing agent decomposes yielding large volumes of non-flammable gases and additional char. The hydration, e.g., addition of water, of calcium aluminate cement of the invention is strongly dependent on temperature. The elevated temperature environment hydrolyzes calcium aluminate cement in the presence of the water, i.e., water vapor is produced in the cement-like char-forming layer. This breakdown is an exothermic reaction through an anhydrous phase.

The hydrolyzed calcium aluminate cement proceeds through a dissolution and precipitation reaction with the silica flour to form a **hardened cementitious structural matrix**, unobtainable by either Vajs or Wortmann, alone or in combination. This adhesive cement structure stays **intact**, and in contrast with the prior art, **remains stable** during extremely high temperatures, supporting the insulating char layer formed by the intumescent additives in concert with the plastic soot, i.e., chiefly carbon produced by the incomplete combustion of the plastic polymer.

After the reaction cycle is complete, the carbonaceous material, supported by the cementitious barrier structure prevents even higher temperatures and high velocity pressure gradients from penetrating the underlying laminate sub-structure. This is a highly desirable effect not possible with the **brittle prior art vitrified** materials.

Note, this is **not** a typical Portland cement reaction that has a long "gel phase to cure." Instead, the water, calcium aluminate cement and silica flour dissolution precipitation reaction occurs very rapidly at elevated temperatures, i.e., elevated kinetics. Neither Vajs nor Wortmann, alone or in combination can ever achieve this unexpected high speed reaction due to the unique combination claimed by the invention, and its unexpected results. The hydrates and structure formed between the reaction of calcium aluminate cement and silica, formed in concert with the water vapor of the intumescent

constituents is indeed unexpected, resulting in a unique ability to protect plastic upon exposure to open flame and high radiant heat.

There is no foundation for the Examiner's statement that, for the claimed invention, workable ranges can be determined by routine experimentation. To the contrary, those of ordinary skill in the art of designing intumescent compositions know that "the development of additives for use with resins remains a highly empirical art. The predictability of the behavior of the final composition is rare to non-existent, see present Application at page 4, lines 6-7.

In contrast, the chemistry of Vajs works as follows. When exposed to high radiant heat or open flame, the ammonium polyphosphate decomposes to form phosphoric acid, which lowers the reaction temperature for the conversion of the pentaerythritol to char and water. Some gases are released by the dicyandiamide. The vitrifying material reflects some IR, until it melts into a **useless glassy film**. As the temperature increases, this film melts and loses stability.

The end result is nothing but a **brittle, fragile carbonaceous** deposition, which is **inconsistent and non-compliant** with current fire safety engineering and fire sciences requirements.

The chemistry of Wortmann's coating produces a fire retardant package dispersed into a film-forming carrier "agent" with the option of including fillers to modify the paint-like coating mix. Wortmann employs the same acid former and char formation mechanism as described by Vajs, thus, the same disastrous results.

Wortmann includes a salt, containing significant quantities of bound water that is supposed to be liberated in the fire insult scenario. The theory with the bound water salt complex is to cool the insulted coating surface at the start of the fire insult exposure, while the intumescent stepwise reaction takes place. After the char forms, only this fragile char and small quantities of residual bound water from the salt complex are relied upon to take on higher velocity flame fronts.

However, higher radiant heat gradients, water impact from high pressure hoses and sprinklers, and the possibility the greater fire-affected environment

in all likelihood will re-ignite the composition, requiring the need for continued fire protection.

The end result of combining Vajs and Wortmann is a material unsuited for today's prescriptive fire and life safety codes and regulatory requirements.

All rejections have been complied with, and applicant respectfully submits that the application is now in condition for allowance. The applicant urges the Examiner to contact the applicant's attorney at phone and address indicated below if assistance is required to move the present application to allowance.

Respectfully submitted,

By: _____
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APPENDIX

AVTEC BSS 7239 Toxic Gas Analysis Test

The results were obtained from a 5/8" thick balsa cored panel with vinyl ester and glass surface skins coated with Thermashield™. The panel was exposed according to the BSS 7239 test protocol for a four minute exposure to 2.5 kW/cm² in the flaming mode. Colorimetric Gas Detection Tubes were used in the toxic gas analysis. The tests were conducted and certified by VTEC Laboratories, Bronx, New York. At no time did the test flame front penetrate the vinyl ester surfaces or corrupt the balsa wood core.

Ambient Temperature 47°F, Relative Humidity 0.65, Bar. Pressure 29.91 in. Hg¹

Gas	Corrected PPM ¹	Corrected PPM ²	Average PPM	Std. Deviation Rail PPM For (PPM)	U.S Passenger Requirements Interior Use
CO	270	200	235	49.497	< 3500
HCN	5	5	5	0	< 150
SO ₂	0	0	0	0	< 100
HCL	1	1	1	0	< 500
HF	0	0	0	0	< 200
NO	40	20	30	14.42	< 100
NO ₂	4	2	3	1.414	< 100

Specimen wgt. 49.7g, ² Specimen wgt. 52.6g 45psi pressure

ASTM E-162 Surface Flammability Test

The results from this test were obtained from cored vinyl ester glass reinforced laminate specimens cured in a press and coated with a 63 mil thick layer of Thermashield™. This test, the Standard Method of Test for Surface Flammability of Materials Using a Radiant Heat Energy Source, is to determine the relative surface flammability performance of various materials under specific test conditions when using a radiant heat source. The results are recorded as a Flame spread Index.

Please refer to the test data and results below. The Flame Spread (Is) is calculated by multiplying the Flame spread Factor (Fs), the speed at which the flame front burns down the specimen, times the Evolution of Heat Factor (Q), determined by the maximum temperature developed in the stack above the burning sample as a result of the burning characteristics of the material under test. NFPA – No. 101 classifies Class A (I) Flame spread to be 0 to 25, Class B (II) Flame spread to be 26 to 75, and Class B (III) Flame spread to be 76 to 100. As indicated below, the test results indicate the laminate panel attained a Class A (I) Flame spread.

E-162 FLAME SPREAD DATA

COMPANY:
 PRODUCT: 81006010
 COLOR: Beige
 DIMENSIONS: 6" X 18"
 THICKNESS: 0.766"
 OBSERVATIONS: No unusual observations.

AL. FOIL ? YES
 EXP TIME: 15 MIN.
 DATE: 12/17/99

TIME TO:	3 INCHES	6 INCHES	9 INCHES	12 INCHES	15 INCHES
SAMPLE #	min.	min.	min.	min.	min.
1	4.88	13.97	-	-	-
2	6.70	8.73	-	-	-
3	7.00	-	-	-	-
4	8.00	-	-	-	-

SAMPLE	Fs	Q	Sample Wt KG	Base Temp deg C	Max Temp deg C	Is INDEX
1	1.31	9.81	1.047	199	251	12.91
2	1.46	7.93	1.033	199	241	11.56
3	1.14	8.49	1.081	199	244	9.71
4	1.12	7.36	1.043	197	236	8.28
AVERAGE:	1.26	8.40	1.051	182	243	10.61

TEST RESULTS

AVG FLAMESPREAD FACTOR (FS) = 1.26
 AVERAGE HEAT OF EVOLUTION (Q) = 8.40
 AVERAGE FLAME SPREAD INDEX (Is) = 10.61
 FLAMESPREAD INDEX RANGE (Is) = 8.28 TO 12.91

ANSI / ASTM E-662 Smoke Generation Density Test

This test, the Standard Test Method for Specific Optical Density of Smoke Generated by Solid Material, is to determine the quantity of smoke generated by solid materials and assemblies in thicknesses up to and including one inch. The test is based on the attenuation (i.e.: change in the concentration) of a light beam by smoke accumulating within a closed chamber. Results are expressed in terms of specific optical density, which is derived from measuring optical density as absorbance within the chamber. The photometric scale used to measure smoke by this method is similar to the optical density scale for human vision.

The test specimens were composite 5/8" thick balsa wood cored vinyl ester laminates fabricated by the SCRIMP process with 1/16" *Thermashield** surface coating on one side. The test method protocol specifies an electrically heated radiant heat source for the non-flaming exposure of the test, and a row of air-propane flamelets to constitute the flaming combustion exposure. The test data and results are illustrated below:

DATE: 12/16/99
PROJECT #:
SUPPLIED BY:
PRECONDITIONING TEMP: 140 deg. F
CONDITIONING TEMP: 70 deg. F
RADIOMETER READING: 7.01 volts
FURNACE VOLTS: 110 volts
BURNER FEUL: 500 cc/min. air; 50 cc/min. propane
SPECIAL PREPERATION: NONE
DESCRIPTION OF MATERIAL:

	NON-FLAMING			FLAMING		
SAMPLE #:	1	2	3	4	5	6
TYPE OF	no	no	no	no	no	no
HOLDER:	trough	trough	trough	trough	trough	trough
THICK(IN.)	0.123	0.123	0.123	0.123	0.123	0.123
WEIGHT(g)	25.4	24.8	26.8	25.4	25.8	25.1
T 100%	1.01E+00	1.01E+00	1.01E+00	1.01E+00	1.00E+00	1.01E+00
T MIN	9.02E-01	9.08E-01	9.21E-01	2.90E-02	4.50E-02	4.50E-02
Tmin %	89.4	90.17	91.64	2.89	4.49	4.47
Dm(20.0 min.)	6.43	5.93	5	203.25	177.95	178.12
T(CLEAR)	9.89E-01	9.92E-01	9.81E-01	8.89E-01	8.89E-01	8.40E-01
Dc(clear)	1.1	0.9	1.4	7	6.9	10.3
Dm(c) (20min.)	5.28	5.07	3.62	196.22	171.03	167.78
Ds(1.5 min.)	1.38	-0.06	0.4	2.57	4.64	4.38
Ds(4.0 min.)	1.38	0.11	-0.23	31.22	20.62	38.38
COLOR OF SMOKE:	GREY	GRAY	GRAY	GREY	GRAY	GRAY

OBSERVATION OF THE BURNING OR SMOLDERING CHARACTERISTICS OF THE SPECIMENS DURING THE TEST SUCH AS DELAMINATION, SHRINKAGE, MELTING, ECT:
OBSERVATIONS:

OPTICAL DENSITY TEST RESULTS SUMMARY

		NON-FLAMING	FLAMING
Ds 1.5 min.	average:	0.6	3.9
Ds 4.0 min.	average:	0.4	30.1
Dm(corr) (20.0 min.)	average:	4.7	178.3